Boston University

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Thesis

IMPROVED METHODS FOR THE PREPARATION OF ALKYL SULFONIC ACIDS

by

Howard Alvin Smith

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Introduction.

Comparatively little is known about alkyl sulfonic acids. Text books and reference books merely state, for the most part, that these acids have been prepared; other books do not even mention them.

A survey of the literature disclosed but very few references to the alkyl sulfonic acids. Ethyl sulfonic acid is supposed to form a deliquescent crystalline mass (1). All the references to the sulfonic acids except the one above are to salts of the acids and not to the free acids themselves. Very little had been done since the time of Strecker(2) and Hemilian(3) until last year when the salts of some alkyl sulfonic acids were prepared by Wagner and Reid(4). However Wagner and Reid give no data on the free sulfonic acids. The separation of the anhydrous acids presents considerable difficulty because of their great hygroscopic tendency.

It was to find a convenient method of preparing the pure anhydrous acids that this work was undertaken.

(1) Cumming, Hopper, and Whelller--Systematic Organic Chemistry Page 323

(2) Strecker--Annalen der Chemie--Vol. 148 Page 92 (1868)

(3) Hemilian--Annalen der Chemie--Vol. 168 Page 146 (1873)

(4) Wagner and Reid--Journal of the American Chemical Society--Vol. 53 Page 3407 (1931)

Preparation of Sodium Butyl Sulfonate.

In the preparation of the sodium butyl sulfonate the work of Zuffanti (1) was closely followed.

100 gm.(.73 mol) of sodium bromide was refluxed with 180 gm.(.72 mol.) of crystallized sodium sulfite ($Na_2SO_3.7H_2O$) dissolved in 400 cc. of water, this being equivalent to 90 gm. of the anhydrous salt. The reaction was complete as shown by the disappearance of the two layers in about 15 hours. The equation for the reaction is

$$C_4H_9Br + Na_2SO_3 = C_4H_9SO_2ONa + NaBr$$

The solution was evaporated to approximately 5/6 of its original volume on the water bath, and on cooling in ice water the sodium butyl sulfonate separated out as a mass of flaky white crystals. By repeating this proceedure about seven fractions were obtained. As was found by Zuffanti the first fractions contained less sodium bromide than did the last, although even the last fraction contained a considerable amount of the sodium butyl sulfonate. On standing the flaky crystals slowly effloresced into a white powder.

The sodium butyl sulfonate was separated from the sodium bromide and any unreacted sodium sulfite by dis-

(1) Saverio Zuffanti--A.M. Thesis, Boston University 1932.

solving the anhydrous sodium butyl sulfonate in absolute alcohol, the inorganic salts being very insoluble in absolute alcohol. The different fractions were ground as finely as possible and dried in the oven at 70°C. for a day. This dry salt mixture was refluxed for about a half an hour with absolute alcohol. The hot solution was quickly filtered using a warm Buchner funnel. The filtrate was then placed in ice water and the precipitated sodium butyl sulfonate filtered out while cold. The sodium butyl sulfonate is quite insoluble in cold absolute alcohol.

The above procedure gave a very pure product, but for most of the following work the unfractionated sodium bromide-sodium butyl sulfonate mixture, obtained by evaporating the original solution to dryness on the water bath, was purified by using ordinary 95% ethyl alcohol. In either case the sodium butyl sulfonate was again powdered and dried for a day at 70°C. as before. This anhydrous salt was used for the preparation of butyl sulfonic acid.

Preparation of Butyl Sulfonic Acid

Anhydrous Ether Method

This method was used byZuffanti(1)with some degree of success although the yields obtained were not stated.

About 15 gm. of the pure anhydrous sodium butyl sulfonate was suspended in 250 cc. of anhydrous ether in a three neck flask equipped with a mercury seal mechanical stirrer. While Zuffanti merely passed in dry hydrogen chloride gas at room temperature until the ether was saturated and then sealed the flask, in these experiments the dry hydrogen chloride gas was passed in intermittently for two days and the solution was continually stirred. The equation for the reaction is

$$C_4H_9SO_2ONa + HCl = C_4H_9SO_2OH + NaCl$$

On the separation of the ether solution and the evaporation of the ether, the yield, even with this improved technique averaged only about 5 gm. Inasmuch as this butyl sulfonic acid contained some dissolved hydrogen chloride gas it was kept in a desiccator containing sodium hydroxide, thus removing the dissolved gas. On standing the acid turned from yellow to a blackish-brown color.

According to Zuffanti butyl sulfonic acid boils

(1) Saverio Zuffanti--A.M. Thesis, Boston University, 1932.

at 68°C. at a pressure of 60 mm. The specific gravity is said to be 1.14 at 22°C. The specific gravity of the butyl sulfonic acid prepared as above was 1.21 at 20°C. Attempts to distill the acid resulted in failure even though the temperature of the oil bath used was as high as 180°C. and the pressure but 35 mm. Attempts to secure a micro boiling point also failed due to the excessive charring of the acid.

Preparation of Butyl Sulfonic Acid Using Ether and Water as Solvents

The preparation of butyl sulfonic acid was next tried by using alcohol-free ether and a small quantity of water. It was hoped that the sodium butyl sulfonate would partly dissolve in the water and react rapidly with the entering hydrogen chloride gas forming the butyl sulfonic acid and sodium chloride, both of which are water soluble. Any excess of sodium chloride would precipitate out and any excess of butyl sulfonic acid would dissolve in the ether.

The alcohol-free ether was prepared by shaking ordinary ether three times with saturated calcium chloride solution. To 200-250 cc. of this ether was added 17-21 gm. of purified sodium butyl sulfonate and 8-15 cc. of water. Dry hydrogen chloride gas was passed in as before. When 15 cc. of water was used all of the sodium butyl sulfonate dissolved, and as the hydrogen chloride gas entered, a white precipitate, later proved to be mostly sodium chloride, settled out. Both the ether and the small water layer turned yellow. The reaction seemed to be complete in about two hours. A three neck flask equipped with a mercury seal mechanical stirrer was used as before.

On separation of the ether layer, drying over anhydrous calcium chloride, and evaporating off the ether about one cc. of butyl sulfonic acid was obtained. Strangely enough this acid did not darken noticeably on standing in the desiccator, but the yield was very poor.

The precipate of sodium chloride was filtered from the water layer which was then placed in a desiccator to dry. The volume decreased from about 20 cc. to 7-8 cc. In attempting to extract the butyl sulfonic acid present with ether an emulsion formed. The ether slowly separated out, and on evaporation of the ether about one cc. of acid was obtained. The remaining ether insoluble layer did not change either red or blue litmus, hence no butyl sulfonic acid was present.

Preparation of Butyl Sulfinic Acid.

The regular Grignard apparatus set-up was used consisting of a three neck flask fitted with a mechanical stirrer, a dropping funnel and a reflux condenser.

12.2 gm. (1/2 mol.) of clean magnesium turnings was placed in a flask and a few iodine crystals were added as a catalyst. 300 cc. of anhydrous ether was added and the solution heated in a water bath up to the boiling point of ether. A mixture of 69 gm. of n-butyl bromide and 100 cc. of ether was added dropwise. The reaction was quite vigorous. The ether was refluxed for twenty minutes after all of the butyl bromide had been added. The solution was cooled in an ice bath and sulfur dioxide was passed in. Enough heat was generated to cause the ether to boil slightly even though it was being stirred in an ice bath. The addition of sulfur dioxide was continued for about 10 minutes after the reaction was complete as indicated by the failure to liberate heat.

The solution was neutralized by the addition of 25.7 gm. (1/4 mol.) of sulfuric acid in 500 cc. of water which served to decompose the addition product. The equations are

$$C_4H_9MgBr + SO_2 = C_4H_9SO_2MgBr$$

$$2C_4H_9SO_2MgBr + 2HOH = 2C_4H_9SOOH + MgBr_2 + Mg(OH)_2$$

The ether layer was separated from the water layer and the ether distilled using a fractionating column. This left a yellow liquid which possessed a very penetrating and lasting "skunk" odor. The yield was around 30 gm.

Preparation of Butyl Sulfonic Acid

Butyl Sulfinic Acid Method.

The following attempts were made to oxidize butyl sulfinic acid to butyl sulfonic acid--a reaction which is said to occur by oxidation when a solution of the acid is exposed to air.

Oxygen was bubbled thru the liquid for an hour but no sulfonic acid was formed. The use of hydrogen peroxide as an oxidizing agent also proved a failure.

Attempts to secure barium sulfonic acid by means of oxidation with barium peroxide were also unsuccessful.

Inasmuch as the oxidation to the sulfonic acid was not accomplished by the above reagents the attempt to prepare butyl sulfonic acid by this method was abandoned.

Preparation of Ethyl Sulfonic Acid

Ammonium Sulfite Method.

This preparation of ethyl sulfonic acid is given in Cumming, Hopper and Wheeler--Systematic Organic Chemistry (1).

10 gm. of ethyl iodide was refluxed with approximately 50 cc. of concentrated ammonium sulfite (2), which contained about 20 gm. (an excess of 11 gm.) of crystallized ammonium sulfite, until all of the ethyl iodide had dissolved. This reaction was complete in about four and one half hours, the solution gradually turning yellow. In a second preparation this yellow solution turned colorless toward the end of the reaction. When ethyl bromide was used about six hours was required for the reaction. the equation for the reaction is:

$$C_2H_5I + (NH_4)_2SO_3 = C_2H_5SO_2ONH_4 + NH_4I$$

About 200 cc. of water was added and the solution boiled vigorously in an open evaporating dish. Yellow litharge was then slowly added with constant stirring in about 3-gram portions, until 15 gm. had been added. The yellow litharge was used because in experiments with ammonium chloride the orange-red gritty litharge would

(1) Cumming, Hopper and Wheeler--Systematic Organic Chemistry, Page 323.

(2) The concentrated solution of ammonium sulfite was freshly made from ammonium hydroxide and sulfur dioxide.

not liberate ammonia, while the yellow reacted fairly readily. It was added slowly because when the required amount was added at one time it reacted for a while but soon lost its activity and no more ammonia was liberated until some fresh litharge had been added. There seems to be no good reason for this peculiarity.

In the first attempts the solution was heated in a round bottom flask by means of an oilbath. The liquid was stirred mechanically. Using this method the time required to drive off all of the ammonia was eight hours. By using the open-dish method the time was reduced to around six hours for a double batch.

The equations for the reactions are:

$$2C_2H_5SO_2ONH_4 + PbO + H_2O = (C_2H_5SO_2O)_2Pb + 2NH_4OH$$

$$2NH_4OH = 2NH_3 + 2H_2O$$

In order to check up on the yield of lead ethyl sulfonate the first batch was evaporated to dryness. It gave a very faint test for ammonia, a negative test for an iodide, and a negative test for a sulfite. The yield of the product was about 15 gm. The theoretical yield based on the 10 gm. of ethyl iodide used is 13.6 gm. The difference between the two yields was due largely to water of crystallization in the lead salt.

The lead ethyl sulfonate was dissolved in water

and the lead was precipitated by passing in hydrogen sulphide gas. This leaves the free acid in solution. The precipitate of lead sulfide was very heavy and it took over an hour for it to be completely precipitated. The solution was tested for completeness of precipitation. After filtering off the precipitate of lead sulfide, the excess hydrogen sulfide was expelled by boiling under reduced pressure.

The solution, free from hydrogen sulfide, was strongly acidic as shown by the reaction with litmus and by the neutralization of a portion with barium carbonate. The ethyl sulfonic acid solution was evaporated on the water bath until all the water was expelled. Damp blue litmus was held in the vapors from time to time to make sure that none of the acid was escaping. The litmus did not change except at the very end of the evaporation when it slowly turned red. The acid was further dried in a sulfuric acid desiccator for three days. The yield was four grams or 59% of the theoretical, ~~that~~ based on the ethyl iodide used. This loss occurred during the concentration of the sulfonic acid solution on the water bath, since the actual yield of acid of another batch was only about 57% of that calculated form the weight of the dried precipitate of lead sulfide which, of course, came from the soluble lead ethyl sulfonate. The acid at this point was a pale yellow in color.

After drying for two days in the desiccator, the acid was fractionally distilled under reduced pressure using the special arrangment of ordinary laboratory equipment described at the end of this thesis. The air admitted thru the capillary was passed thru a drying train of two sulfuric acid wash bottles. A trap was placed between the bottles and the capillary to catch any sulfuric acid spray. It was necessary to use a sand bath to heat the flask. The acid in the flask charred considerably due probably to the presence of water, as about 2cc. of water came over before the sulfonic acid began to boil. The boiling point ef the acid was about 184°C at 37 mm. The distilled acid was a pale brown viscous liquid. Its specific gravity was 1.199 and its micro boiling point 201° C. The acid charred slightly in heating to this temperature.

Cumming Hopper and Wheeler(1) state that "ethyl sulfonic acid is stable and forms a deliquescent crystalline mass" and give as a reference "Berichte der Deutschen Chemischen Gesellschaft--Vol. 15 page 445. In looking up this reference it was found that it dealt with the stability of the acids when treated with hydrochloric acid but made no mention of the acid existing as a deliquescent crystalline mass.

(1) Cumming, Hopper and Wheeler--Systematic Organic Chemistry Page 323.

Although the distilled acid was cooled to 0°C no crystals separated out. Hence it would seem as if ethyl sulfonic acid is a liquid as is pure butyl sulfonic acid, the preparation of which is described in the following pages of this thesis.

Preparation of Butyl Sulfonic Acid

Ammonium Sulfite Method.

137 gm. (1 mol.) of butyl bromide was refluxed with 350 cc. of ammonium sulfite solution (1) containing about 175 gm. of crystallized ammonium sulfite. After 22 hours very little had reacted, so more ammonium sulfite solution was added--containing approximately 85 gm. of the salt. Considerable bumping occured and at times it was so violent that some of the butyl bromide escaped. After refluxing 19 more hours--a total of 41 hours-- the butyl bromide layer had completely disappeared. The equation is

$$C_4H_9Br + (NH_4)_2SO_3 = C_4H_9SO_2ONH_4 + NH_4Br$$

500cc. of water was added and this solution, as in the preparation of ethyl sulfonic acid, was boiled with yellow litharge in an open evaporating dish. As with the heating of ammonium ethyl sulfonate and litharge an oil bath and mechanical stirrer were first used, the solution being in a liter round-bottom flask. After boiling 40 hours a large amount of ammonia was still present. A white precipitate which formed when silver nitrate was added to a small portion of the cold filtered solution showed the continued presence of ammonium bromide. After boiling but 4 hours in the open evaporating

(1) The concentrated ammonium sulfite solution was freshly made from ammonium hydroxide and sulfur dioxide.

dish all the ammonia had been liberated, and a negative halogen test showed that the ammonium bromide had all reacted. It was filtered while hot and on cooling a very large precipitate of lead bromide formed. The solution was cooled in an ice bath and filtered. The reactions are

$$2C_4H_9SO_2ONH_4 + PbO = (C_4H_9SO_2O)_2Pb + 2NH_3 + H_2O$$

$$2NH_4Br + PbO = PbBr_2 + 2NH_3 + H_2O$$

Hydrogen sulfide was passed into the solution until all of the lead salt had reacted. This took an hour even though the solution was warm. The lead sulfide was filtered off (when dried it weighed about 20 gm.) and the resulting clear solution tested for a bromide and for lead. A negative test was secured in each case. The volume of the solution being about 800 cc., it was evaporated directly over an open flame. When fairly concentrated it was evaporated on the water bath until no more water vapor came off. The butyl sulfonic acid was dried in an ordinary desiccator ten days, then in a vacuum sulfuric acid desiccator for three days. It was then fractionally distilled under vacuum (see description and diagram at the end of this thesis), ~~heated on a sand bath~~ ~~in~~ using a 125 cc. Claisen flask which was heated on a sand bath. The air admitted through the capillary was dried by passing through two wash bottles

containing sulfuric acid and thru another bottle which acted as a trap to catch any sulfuric acid spray. About 4 cc. of a water-white non-viscous liquid came over from 50° to 60° C. at 27 mm. even though the liquid did not boil. When the liquid began to boil the temperature rose rapidly to 172° C. where it remained constant as long as the pressure was 10 mm. As the pressure dropped to 7 mm. the boiling point dropped to 167° C where it remained constant thruout the distillation. The distillate was water-white as it dripped into the condenser, but possessed a very faint brownish tinge as it collected in the separatory funnel. On standing a few days, even though completely sealed, the liquid darkened noticeably. Almost no residue was left in the Claisen flask after the distillation. The final yield of pure acid was about 18 gm.

Attempts to secure a micro boiling point failed because of the excessive charring of the acid around 275 C.

Micro specific gravity determinations gave the following results

(1)---1.200
(2)---1.199
(3)---1.189

Neutral equivalent determinations gave very close checks with the calculated value which is 138. The values obtained were

(1)---138.7
(2)---139.7
(3)---139.1

The second and third samples after the titration with sodium hydroxide were quantitatively divided by means of a 100 cc. gas collection tube.. These portions were evaporated to dryness on the water bath and the sodium salt thus obtained was used for sulfur determinations. Inasmuch as it was impossible to scrape out every trace of the sodium salt the weight of the small amount left in the beaker was determined by weighing the beaker and the unremoved residue, dissolving the sodium salt and reweighing the beaker. The weight of the acid represented by the weight of the sodium salt was calculated and subtracted from the weight of butyl sulfonic acid in the solution which was evaporated. The corrections were of the order of .004-.005 gm. on a .2 gm. sample. Thus the actual weight of butyl sulfonic acid (in the form of the sodium salt) used in the Parr bomb was determined. Applying this correction, the sulfur determinations were as follows

(1)---23.1%
(2)---23.2%
(3)---23.2%

The calculated per cent of sulfur in butyl sulfonic acid is 23.2. The above results check unusually well. The

sodium salt was necessarily used since the free acid would have reacted with the sodium peroxide which was used as the oxidizing agent in the bomb.

A direct refractive index was not taken because it was considered unwise to use the acid on the metal plates of the Abbé refractometer. A rough determination was made by the use of a microscope and solids of known refractive indices in which the Becke lines were visible. The refractive index was found to be between 1.571 (barium nitrate)and 1.640(ammonium chloride). The only other standard between the above is sodium bromide (1.617)but this salt was not available.

This butyl sulfonic acid was used to prepare butyl sulfonanilide and p-toluidine butyl sulfonate.

Preparation of Butyl Sulfonanilide

Thionyl Chloride Method

The anilide of butyl sulfonic acid was made by adding aniline to an ether solution of butyl sulfonyl chloride. The butyl sulfonyl chloride was made from butyl sulfonic acid and thionyl chloride. Thionyl chloride is the best reagent to form the acid chloride since the products formed, other than the acid chloride, are water, sulfur dioxide, and possibly hydrogen chloride. The last two, with any unreacted thionyl chloride, can be removed by boiling. Its advantage over phosphorous pentachloride is readily obvious.

To 2.1 cc. of butyl sulfonic acid in a six inch test tube 1.3 cc. of thionyl chloride was slowly added. The test tube was shaken and then heated gently with an open flame. It was then equipped with a short length of glass tubing which acted as a condenser and heated in boiling water for 30 minutes. Two equations are given for the formation of an acid chloride from thionyl chloride and an acid. In the reaction as given in Cumming, Hopper and Wheeler two molecules of acid react with one molecule of thionyl chloride(1). If this is true the equation for

(1)Cumming, Hopper and Wheeler--Systematic Organic Chemistry Page 323,(1924 Edition).

the reaction is

$$2C_4H_9SO_2OH + SOCl_2 = 2C_4H_9SO_2Cl + SO_2 + H_2O$$

Other authors state that they react in a 1 : 1 ratio.

$$C_4H_9SO_2OH + SOCl_2 = C_4H_9SO_2Cl + SO_2 + HCl$$

The quantities were chosen so that an excess of either reagent was avoided, provided the 2 : 1 ratio is correct. The butyl sulfonyl chloride was cooled, and diluted with 150 cc. of anhydrous ether, and the theoretical amount of freshly distilled aniline (1.9 cc.) was slowly added with constant stirring. A white flaky precipitate immediately formed. The precipitate was filtered by suction. A small second crop of crystals slowly settled out from the ether. The yield was 3.4 gm. or 85 % of the theoretical yield. The equation is

$$C_4H_9SO_2Cl + C_6H_5NH_2 = C_4H_9S(=O)_2-N(H)-C_6H_5 + HCl$$

The crystalline product was dried on a filter paper after which a portion was dried in the oven for an hour at 70-80° C. On heating, the crystals turned slightly brown in color. Each set of crystals, whether heated or unheated, melted at 122-3° C. into an opaque mass which definitely melted into a liquid at about 135° C. The

crystals gave a positive test for both nitrogen and sulfur. They were extremely soluble in water, ethanol and butanol, but were insoluble in hot or cold ether, carbon tetrachloride, chloroform, ligroin, benzene and toluene.

It was hoped that the product might be recrystallized from a mixture of a solvent and a non-solvent. Various ethanol-ether and ethanol-carbon tetrachloride mixtures were made but the difference in solubility of the product in the hot and cold mixtures made recrystallization impossible.

Analysis of the butyl sulfonanilide for sulfur by the Parr bomb method gave 9.2 and 9.5%. The theoretical percent of sulfur is 15.0. Analysis for nitrogen gave 9.01%, while the theoretical percent is 6.57. Hence the product was impure and the impurity was a nitrogen compound.

It was suspected that aniline hydrochloride might have formed from the excess aniline and the hydrogen chloride (formed with the sulfonanilide). If this were the case the solution would be acidic to litmus. On testing with litmus the solution was found to be acidic, and considerable ammonium hydroxide was required to make it neutral. It also gave a positive test for a chloride.

Attempts made to purify this mixture resulted in failure. The anilide solution was made slightly ammo-

niacal to liberate the aniline from the aniline hydrochloride. The small quantity of aniline was extracted thrice with ether. The solution was made very slightly acidic with dilute hydrochloric acid and divided into two portions. One was evaporated to dryness on the water bath while the other was allowed to evaporate in a vacuum desiccator. In both cases the resulting solid was pale brown in color. The alcohol soluble portion was extracted thrice with absolute alcohol. A white precipitate of ammonium chloride was left as a residue. On evaporation of the absolute alcohol to dryness at room temperature, the solid formed was still pale brown in color. Attempts to remove the color by washing the finely powdered solid with non-solvents were unsuccessful although benzene removed a small amount of colored material. The solid was then dissolved in hot absolute alcohol in which it was difficultly soluble although the original precipitate was very soluble in cold absolute alcohol. Purified bone black was added and the mixture filtered. On evaporation to dryness at room temperature the product was still colored.

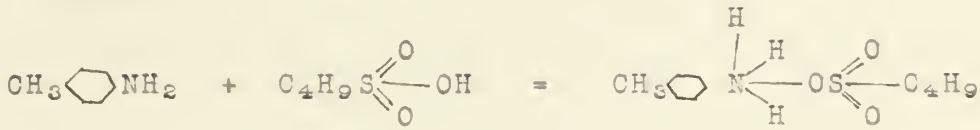
This product darkened but did not melt up to 220° C. (original material melted at 122-3° C.). A qualitative analysis showed the presence of a large amount

of sulfur as the hydrogen sulfide odor was very distinct. A negative nitrogen test was secured. It gave a positive test for ammonia(using concentrated sodium hydroxide), but a negative test for a chloride and sulfate. Thus the butyl sulfonanilide even by the above mild treatment had decomposed and the above product was undoubtedly ammonium butyl sulfonate.

Preparation of p-Toluidine Butyl Sulfonate

It was next decided to find out if p-toluidine would form a salt with butyl sulfonic acid and if the p-toluidine butyl sulfonate thus formed could be used as a derivative.

To about .8 cc.(a slight excess)of butyl sulfonic acid dissolved in about 100 cc. of anhydrous ether was added dropwise and with constant stirring a solution of .70 gm. of p-toluidine in 25 cc. of anhydrous ether. The white stringy precipitate which immediately formed was filtered by suction and washed with several portions of anhydrous ether. It was placed on the top of the desk to dry. However it soon commenced to turn yellow, hence it was dried in a vacuum desiccator. It was not recrystallized as both reactants were ether soluble and no side reactions could occur. The yield was 1.4 gm. or 87.5% of the theoretical yield. The equation for the reaction is



The p-toluidine butyl sulfonate was pale yellow in color, but when finely powdered it was white. It had a very soapy feeling and was soluble in alcohol and water. The melting point was not sharp and depended

somewhat upon the rate of heating. It always commenced to melt at 89°C. but did not completely melt except at a higher temperature. When heated fairly rapidly it would completely melt at 93°C. but when heated very slowly it did not melt until a temperature of 99°C. was reached.

A qualitative analysis showed the presence of both nitrogen and sulfur. A quantitative sulfur determination by the Parr bomb gave 13.5%. This is a good check since the calculated amount of sulfur is 13.1%. Quantitative nitrogen determinations gave 5.22 and 5.44%. This, too, is a good check since the theoretical percent of nitrogen is 5.71.

The p-toluidine butyl sulfonate is easy to prepare in a pure form, but the lack of a definite melting point makes it a rather hard derivative to identify easily.

Preparation of the Sodium Sulfonate Salt from "Propylene Chlorohydrin"

Eastman Kodak's "propylene chlorohydrin" was assumed by Zuffanti (1) to be 1-chloro propanol-2. In this work the preparation of the sodium sulfonate salt was undertaken on this assumption. However, in the literature it was noted that propylene chlorohydrin was used to apply to either 1-chloro propanol-2 or 2-chloro propanol-1. The Index of Chemical Abstracts lists "propylene chlorohydrin" as 2-chloro propanol-1.

In answer to an inquiry, the Eastman Kodak Company stated that their "propylene chlorohydrin" was probably a mixture of 1-chloro propanol-2 and 2-chloro propanol-1 as it was prepared by treating propylene glycol with hydrochloric acid.

The sodium sulfonate salt of the above-mentioned "propylene chlorohydrin" was prepared by refluxing 21 gm. with 50 gm. of crystallized sodium sulfite in 85 cc. of water. The reaction was complete after refluxing for fifteen hours as evidenced by the disappearance of the two layers. This solution was fractionally crystallized. The first fractions were very inorganic in appearance

(1) Saverio Zuffanti--A. M. Thesis, Boston University, 1932.

and only a very small portion dissolved in boiling absolute alcohol. The later fractions were yellowish pasty crystals and nearly completely soluble in absolute alcohol. Thus, in this case, the sodium sulfonate salt was more soluble in water than the sodium chloride formed, whereas the sodium butyl sulfonate was less soluble than sodium bromide or sodium chloride. The sodium sulfonate salt from the "propylene chlorohydrin" would be expected to be more soluble than sodium butyl sulfonate since it contains one less carbon atom and is an alcohol.

Preparation of Pure 1-Bromo-Propanol-2

Inasmuch as the desired acid was 1-sulfo-propanol-2 (that compound contains an asymmetric carbon atom and would therefore be optically active) it was necessary to prepare some pure 1-chloro-(or bromo-) propanol-2. A survey of the literature disclosed a method of making pure 1-bromo-propanol-2 from allyl bromide and sulfuric acid using a small amount of copper sulfate as a catalyst, (1). The allyl bromide was prepared and purified according to the directions given in Organic Syntheses (2). The 1-bromo-propanol-2 was prepared as follows; To 313 gm. of allyl bromide in a five liter flask, a mixture of 600 gm. of sulfuric acid (66°Be) and 5 gm. of crystallized copper sulfate was added in very small portions, the flask being stirred by a mechanical stirrer and cooled with ice water. The reaction was very violent and but small quantities of the sulfuric acid mixture could be safely added otherwise considerable charring would occur. The reaction was complete in two hours. Three liters of water was then added and the mixture was distilled as long as the distillate separated into two layers when saturated with potassium carbonate. This distillation took six hours. The dis-

(1) Bull. de la Soc. Chim. Belg. Vol. 39, 87-90 (1930)

(2) Organic Syntheses. Vol. 1, page 3.

tillate was extracted thrice with ether and the ether dried over potassium carbonate. The ether was distilled off and the remaining liquid fractionated. Most of the liquid came over at 148°C. the boiling point of 1-bromo-propanol-2. The yield was 80 gm. The yield could be increased by adding the sulfuric acid mixture more slowly.

The equation for the reaction is

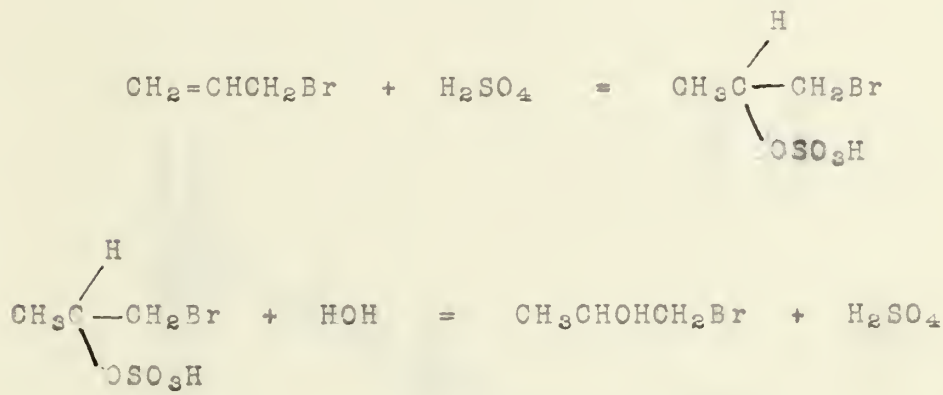
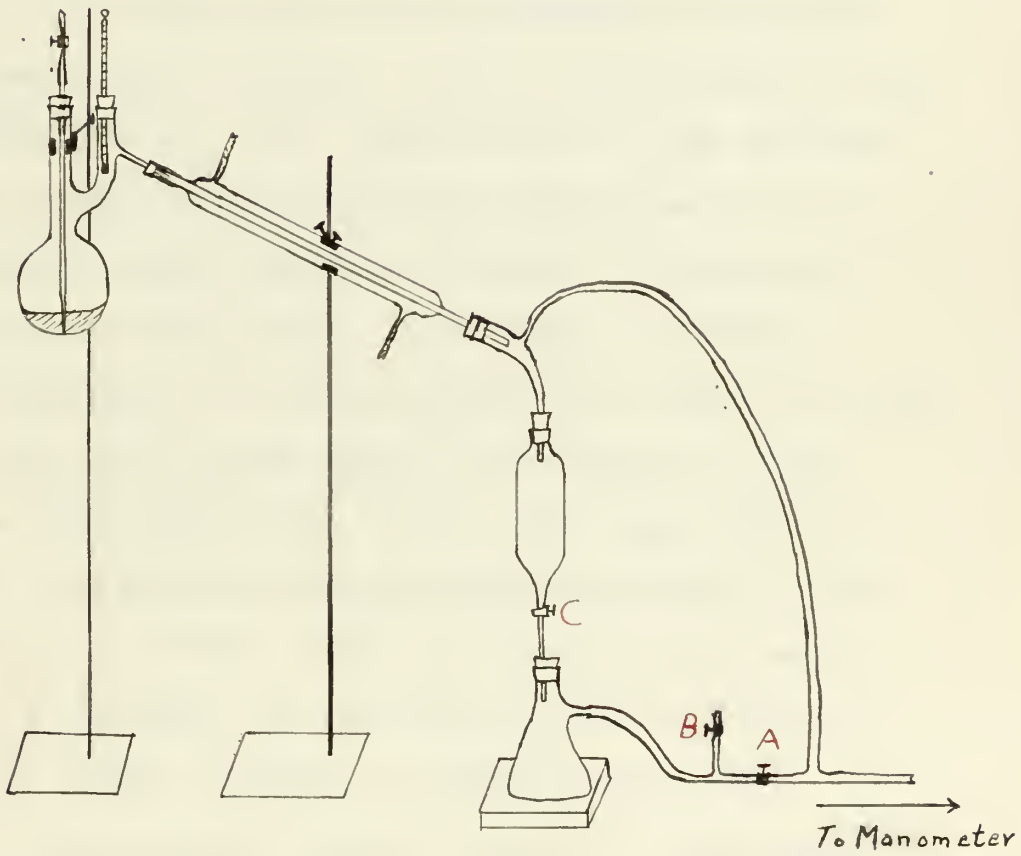


Diagram of

Fractional Distillation Apparatus

For Reduced Pressure



Apparatus for Fractional Distillation Under Reduced Pressure.

For laboratories having no equipment for fractional distillation under reduced pressure the following apparatus has been devised. The parts are included in ordinary organic chemistry equipment. The whole apparatus can be quickly assembled. A diagram is given on the preceeding page.

The distilling end of the condenser is attached to a Claisen flask as usual, the air being admitted thru the capillary tube. The receiving end of the condenser is fitted with a side-arm adapter the bottom of which extends into a small separatory funnel. This in turn extends into a filter flask which sets on a wooden block on the desk. For the collection of small fractions a small test tube can be fitted in a hole in a cork and placed into the filter flask. For large fractions the filter flask is the actual receiving vessel. The side arm of the filter flask is connected by pressure tubing to a "T" tube, to one end of which is attached a piece of rubber tubing and a Hoffman screw (B). The other end connects with the tubing from the side- arm adapter by means of another "T" tube, Between the two "T" tubes is another Hoffman screw (A).

While the fraction is collecting the screw (A) is open and the screw (B) and the stopcork (C) are closed. When the desired fraction has collected (C) is opened and the liquid run into the receiving flask. (C) is then closed, (A) is closed and (B) is opened. It is necessary to remove the vacuum in the filter flask by opening (B) before the filter flask can be removed. If desired a 2-hole stopper could be used to connect the filter flask to the separatory funnel and the air admitted thru a right angle bend fitted with a rubber tube and screw as in (B). The block under the filter flask is slid to one side and the flask is removed. A clean test tube is placed in the flask which is replaced under the separatory funnel. (B) is then closed and (A) is slowly opened. If(A) is opened slowly the pressure will not change but a few mm. and of course as soon as all the air is withdrawn it goes back to the original pressure. Thus while one fraction is being removed another is collecting in the separatory funnel and the vacuum is not destroyed at any time.

In case it is necessary to distill in a moisture free air (as is the case with the sulfonic acids) the air admitted into the Claisen flask can be dried with sulfuric acid wash bottles. That admitted at (B) to release the pressure can be dried by a calcium chloride tube.

Summary

This investigation of the methods of preparing sulfonic acids has shown that the ammonium sulfite method gives the best yield of a pure product.

The method of preparing sulfonic acids by the action of dry hydrogen chloride gas on an ether suspension of the sodium salt met with but little success. Modifications of this method were also unsuccessful. The sulfinic acid method was unsuccessful because the sulfinic acid could not be oxidized to the sulfonic acid.

Pure ethyl and butyl sulfonic acids have been prepared. The purity and physical constants of butyl sulfonic acid have been accurately determined and found to check with the theoretical values. Butyl sulfonanilide and p-toluidine butyl sulfonate have been prepared and identified.

Pure 1-bromo-propanol-2 has been prepared and is available for future use in preparing 1-sulfo-propanol-2.

A new arrangement of apparatus for fractional distillation under reduced pressure has been devised which permits the collection of fractions without breaking the vacuum. It is composed of the regular organic desk equipment and is easily and quickly assembled. It is adaptable to the collection of both large and small volumes of liquid.

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